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(54) CUBIC BORON NITRIDE-CONTAINING SINTERED COMPACT AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain the subject dense sintered compact with its wear resistance retained, improved in esp. chipping resistance and fracture toughness by reactive- sintering properly selected components of the binding phase composition with regulated particle sizes.

CONSTITUTION: This sintered compact is composed of 10-70vol.% of cubic boron nitride and a binding phase consisting mainly of ceramics as the residual part with inevitable impurities. The binding phase is composed of, based on the final sintered compact, 5-30vol.% of aluminum oxide $\leq 1\mu\text{m}$ in particle diameter, 3-20vol.% of aluminum nitride and/or aluminum boride, 10-40vol.% of at least one kind selected from titanium carbide, titanium nitride and titanium carbonitride and 3-30vol.% of titanium boride. Thereby, this sintered compact has the following advantages superior to the conventional products of this kind of sintered compact: higher in fracture toughness; excellent in thermal shock resistance, chipping resistance at elevated temperatures and oxidation resistance; therefore, having longer service life when used as a cutting tool.

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CLAIMS

[Claim 1] A sintered compact consisting of 10-70 vol.% cubic boron nitride and the rest that is a binding phase consisting mainly of ceramics and included impurities, wherein the binding phase consists of 5-30 vol.% of aluminum oxide with particle diameter of $1\mu\text{m}$ or less, 3-20 vol.% of aluminum nitride and/or aluminum boride, 10-40 vol.% of at least one substance selected from titanium (Ti) carbide, Ti nitride and Ti carbon-nitride, and 3-30 vol.% of Ti boride, all based on the volume of the final sintered compact.

[Claim 2] A cubic boron nitride-containing sintered compact as in Claim 1, wherein the cubic boron nitride is surrounded by a layer of Ti compound(s), such as Ti boride and/or Ti nitride, with a mean layer thickness of 0.1-2.0 μm .

[Claim 3] A sintered compact consisting of 10-70 vol.% cubic boron nitride and the rest that is a binding phase consisting mainly of ceramics and included impurities, wherein the binding phase consists of 5-30 vol.% of aluminum oxide with particle diameter of $1\mu\text{m}$ or less, 3-20 vol.% of aluminum nitride and/or aluminum boride, 10-40 vol.% of at least one substance selected from Ti carbide, Ti nitride and Ti carbon-nitride, 3-30 vol.% of Ti boride, and not more than 40 vol.% of carbide or nitride of metals of Groups 4a, 5a and 6a of the Periodic Table or their mutual solid solutions (excluding carbide, nitride and carbon-nitride of Ti), all based on the volume of the final sintered compact.

[Claim 4] A cubic boron nitride-containing sintered compact as in Claim 3 wherein, the cubic boron nitride is surrounded by a layer of Ti compound(s), such as Ti boride and/or Ti nitride, with a mean layer thickness of 0.1-2.0 μ m.

[Claim 5] The process of preparing cubic boron nitride-containing sintered compact, comprising Step 1 in which a powder mixture consisting of cubic boron nitride powder, a powder of at least one oxygen-containing compound selected from carbide oxide, nitride oxide and carbon-nitride oxide of Ti, and Al powder, is made into a green compact; Step 2 in which the green compact is heat-treated if necessary at 700-1000°C in a 1×10^{-3} Torr or higher vacuum; and Step 3 in which the compact is reactive-sintered under the super high pressure and temperature of 4-6GPa and 1400-1600°C to obtain a sintered compact consisting of 10-70 vol.% cubic boron nitride, 5-30 vol.% of aluminum oxide with a particle diameter of 1 μ m or less, 3-20 vol.% of aluminum nitride and/or aluminum boride, 10-40 vol.% of at least one substance selected from Ti carbide, Ti nitride and Ti carbon-nitride and 3-30 vol.% of Ti boride.

[Claim 6] The process of preparing cubic boron nitride-containing sintered compact as in Claim 5 wherein, the proportion of elemental oxygen is 0.2-0.8 moles per mole of non-metallic elements in the aforesaid powder of the oxygen-containing compound.

[Claim 7] The process of preparing cubic boron nitride-containing sintered compact, comprising Step 1 in which a powder mixture consisting of cubic boron nitride powder, a powder of at least one oxygen-containing compound selected from carbide oxide, nitride oxide and carbon-nitride oxide of Ti, aluminum powder, and at least one powder selected from carbides and nitrides of Group 4a, 5a and 6a metals of the Periodic Table and their mutual solid solutions, is made into a green compact; Step 2 in which the green compact is heat-treated if necessary at 700-1000°C in a 1×10^{-3} Torr or higher vacuum; and Step 3 in which the compact is reactive-sintered under the super high pressure and temperature of 4-6GPa and 1400-1600°C to obtain a sintered compact consisting of 10-70 vol.% cubic boron nitride, 5-30 vol.% aluminum oxide with a particle diameter of 1 μ m or less, 3-20 vol.% aluminum nitride and/or aluminum boride, 10-40 vol.% of at least one substance selected from Ti carbide, Ti nitride and Ti carbon-nitride, 3-30 vol.% Ti boride and not more than 40 vol.% carbide or nitride of 4a, 5a and 6a Group metals of the Periodic Table or their mutual solid solutions (excluding carbide, nitride and carbon-nitride of Ti).

[Claim 8] The process of preparing cubic boron nitride-containing sintered compact as in Claim 7 wherein, the ratio of elemental oxygen is 0.2-0.8 moles per mole of non-metal elements in the aforesaid powder of oxygen-containing compound done.]

[Detailed Description of the Invention]

[0001]

[Industrial Application] Specifically, this invention relates to the cubic boron nitride content sintered compact optimal as a cutting tool or an antifriction tool, and its manufacture method about the cubic boron nitride content sintered compact which is a high degree of hardness and has a high fracture toughness value, and its manufacture method.

[0002]

[Description of the Prior Art] Cubic boron nitride has the high degree of hardness which ranks second to a diamond, and the outstanding thermal conductivity, and has the advantage which was moreover excellent as a tool material that compatibility with iron is low compared with a diamond. There are JP,56-156738,A, JP,58-58247,A, JP,58-60678,A, JP,58-60679,A, JP,58-60680,A, and JP,2-208259,A as a typical thing which much examination about the cubic boron nitride content sintered compact which becomes by the cubic boron nitride and the binder phase of a metal or ceramics which have this outstanding advantage is performed, among those is proposed from the organization of binder-phase component composition and a sintered compact.

[0003]

[Problem(s) to be Solved by the Invention] In JP,56-156738,A, by the volume ratio, 20 - 80% of cubic boron

nitride. The 1st binder phase of the carbide of remaining periodic-table the 4a, 5a, and 6a group metal, a nitride, a boride, silicides, such mixture, or a mutual solid-solution compound. It considers as the 2nd binder phase of the alloy containing aluminum, Si, nickel, Co, Fe, or these, and a compound. The sintered compact for high degree-of-hardness tools with which the compound of nothing and aforementioned periodic-table the 4a, 5a, and 6a group metal becomes at 50% or more by the volume ratio in a binder phase about the binder phase which the 1st binder phase and the 2nd binder phase followed all over the sintered-compact organization is indicated.

[0004] The sintered compact for high degree-of-hardness tools given in this official report contains quite a lot of oxygen in the fines below the micron used as a raw material, or a micron. Although it is said using the carbide of Ti, Zr, and Hf of non-chemistry **** composition, a nitride, and a charcoal nitride to oxygen reducing a degree of sintering to the bottom of extra-high voltage that the degree of sintering was raised without carrying out the generation of gas From the kind and particle size of the method of the combination of the 1st binder phase and the 2nd binder phase, and aluminum compound as the 2nd binder phase, it has not resulted and there is a problem that a fracture toughness value is low by the time abrasion resistance and body deficit nature are still satisfied.

[0005] In JP,2-208259,A, the hard phase 20 of cubic boron nitride and/or wurtzite type boron nitride - 90 volume %, The remainder consists of a binder phase and an unescapable impurity. this binder phase At least one sort in the nitrides of 4a and 5a of a periodic table, and 6a group metal, and these mutual solid solutions, At least one sort in the borides of 4a and 5a of a periodic table, and 6a group metal, and these mutual solid solutions, The high-density phase boron nitride reaction-sintering object which contains at least one sort in an aluminum oxide, HOU-ized aluminum, aluminum nitride, silicon carbide, and silicon nitride in others is indicated.

[0006] Although the high-density phase boron nitride reaction-sintering object of a publication carries out reaction sintering of the metals of 4a and 5a of boron nitride and a periodic table, and 6a group, and two or more sorts of these alloys to this official report and being considered as the high-density boron nitride sintered compact the positive consideration to oxygen like above-mentioned JP,56-156738,A is made -- **** -- high -- when degree of hardness hardening network and alloy cast iron are cut as *-ed material, there is [that abrasion resistance and deficit-proof nature have come to be satisfied] a say problem

[0007] In JP,58-58247,A and JP,58-60680,A, cubic boron nitride is surrounded by the boride of Ti, Zr, Hf, and Mo which becomes by the average layer thickness of 0.1-2 micrometers, the cubic boron nitride sintered compact which ceramics and the metal otherwise contained is indicated, to JP,58-60678,A and JP,58-60680,A, cubic boron nitride is surrounded by the nitride of Ti, Hf, and Si which becomes by the average layer thickness of 0.1-2 micrometers, and the cubic boron nitride sintered compact which ceramics and the metal otherwise contained is indicated.

[0008] The cubic boron nitride sintered compact indicated by the official report of these four affairs Although it is said that it is the sintered compact which the void by the minute depression in the front face of a cubic boron nitride particle etc. was lost, was excellent in the adhesion of cubic boron nitride and a binder phase, and combines toughness and abrasion resistance by surrounding the front face of a cubic boron nitride particle by the binder phase There is a problem that a fracture toughness value and the deficit-proof nature at the time of an elevated temperature still are not enough, and become a short life.

[0009] this invention is what solved the above troubles, and it aims at offer of the cubic boron nitride content sintered compact which succeeded in raising deficit-proof nature and a fracture toughness value, and its manufacture method, without reducing abrasion resistance from selection of a binder-phase composition component, and manufacture of the particle size while specifically selecting binder-phase precursor matter which carries out reaction sintering to cubic boron nitride and making it a precise sintered compact by reaction sintering.

[0010]

[Means for Solving the Problem] When this invention persons are considering improvement in the abrasion resistance of the sintered compact which becomes by cubic boron nitride and the binder phase, and deficit-proof nature, as a starting material for producing a sintered compact On the binder-phase precursor matter and concrete target which do reaction sintering to cubic boron nitride If it has by the binder-phase precursor matter and cubic boron nitride and reaction sintering is made to start using the binder-phase precursor matter of one or

more sorts and aluminum of the carbonation object of Ti, a nitric oxide, and a charcoal nitric oxide The knowledge that it is precise and the sintered compact excellent in abrasion resistance, deficit-proof nature, and the fracture toughness value is obtained is acquired, and it comes to complete this invention.

[0011] Namely, the sintered compact of this invention is a volume ratio, it is the sintered compact which consists of 10 - 70% of cubic boron nitride, and the binder phase which makes the remaining ceramics a principal component and an unescapable impurity, and this binder phase is the whole sintered-compact ratio. 5 - 30% of aluminum oxides, and aluminum nitride and/or 3 - 20% of HOU-ized aluminum. It consists of 10 - 40% more than per sort in a titanium carbide, a titanium nitride, or a charcoal titanium nitride, and 3 - 30% of titanium borides, and this aluminum oxide is characterized by the bird clapper with the particle size of 1 micrometer or less.

[0012] The binder phase in the sintered compact of this invention An aluminum oxide, and aluminum nitride and/or HOU-ized aluminum, It consists of one or more sorts and titanium boride in a titanium carbide, a titanium nitride, or a charcoal titanium nitride. Furthermore, the need is accepted. The carbide of periodic tables 4a and 5a and 6a group metal, a nitride, a boride, silicides, and these mutual solid solutions one or more sorts in (however, removing the carbide of Ti, a nitride, and a charcoal nitride) -- one or more sorts in below 40 volume % or metals, such as Fe, Co, nickel, Cr, Mo, and W, and an alloy -- it contains When making a metal and an alloy contain the inside of this, and in a binder phase, a wear-resistant fall is below 10 volume % preferably below 30 volume % in [a bird clapper to] a binder phase notably.

[0013] If an aluminum oxide becomes under 5 volume % by the whole sintered-compact ratio among the constituents of a binder phase If a wear-resistant and heat-resistant fall is remarkable and increases exceeding 30 volume % conversely If the fall of toughness becomes remarkable and aluminum nitride and/or HOU-ized aluminum become under 3 volume % If the fall of intensity and toughness will become remarkable if it is hard to become a precise sintered compact and increases exceeding 20 volume % conversely, and one or more sorts of a titanium carbide, a titanium nitride, and a charcoal titanium nitride become under 10 volume % If the fall of intensity and toughness is remarkable and increases exceeding 40 volume % conversely Other binder-phase component contents decrease relatively, and if a heat-resistant and wear-resistant fall is remarkable, a hot on-the-strength fall is remarkable when a titanium boride becomes under 3 volume %, and it increases exceeding 30 volume % conversely, the intensity in the temperature field which is not not much high, and the fall of toughness will become remarkable.

[0014] The cubic boron nitride in the sintered compact of this invention If it increases exceeding 70 volume %, a binder phase will become under 30 volume % relatively. in order it is weak, for the effect in consideration of the composition component of a binder phase to surround the particle of many cubic boron nitride with Ti compound of a titanium boride and/or a titanium nitride as it can do especially, and to raise the intensity and the toughness of a sintered compact If the content of cubic boron nitride has [a relation with particle size] desirable 70 volume % with a certain thing and cubic boron nitride becomes under 10 volume % conversely, the high degree of hardness of cubic boron nitride cannot fully be utilized thoroughly, and the wear-resistant fall of a sintered compact will become remarkable.

[0015] Although it can also have and produce by various kinds of manufacture methods currently performed from the former in order to produce the sintered compact of this invention, when it carries out by the following method, it is desirable [that it is precise and the sintered compact of high intensity quantity toughness is easy to be obtained].

[0016] this invention is characterized by providing the following in the manufacture method of a sintered compact. Cubic boron nitride powder At least one sort of oxygen content compound powder in the carbonation object of Ti, a nitric oxide, and a charcoal nitric oxide The 3rd process which heat-treats this powder-compacting Plastic solid at 700 degrees C - 1000 degrees C among the vacuum of 1×10^{-3} or more Torrs if needed [the 1st process and if needed] which make the end of mixed powder it becomes with aluminum powder a powder-compacting Plastic solid and which subsequently has and carries out reaction sintering the 2nd process at a pressure 4 - 6GPa, and an extra-high voltage elevated temperature with a temperature of 1400-1600 degrees C

[0017] The oxygen content compound powder in the manufacture method of the sintered compact of this invention It is the important factor to which reaction sintering by cubic boron nitride powder and aluminum

powder is made to perform. specifically Have by reaction sintering of oxygen content compound powder and aluminum powder, and the oxygen and aluminum in oxygen content compound powder join together. Reaction sintering of the other elements and cubic boron nitride become an aluminum oxide and excluding the oxygen in oxygen content compound powder further. Or by making reaction sintering of other elements and cubic boron nitride except the oxygen in oxygen content compound powder, and aluminum perform sintering -- an aluminum oxide, aluminium nitride and/or hoe-sized aluminum, and one or more sorts and titanium boride in a titanium carbide, a titanium nitride, and a charcoal titanium nitride are contained as a binder phase in the living body

[0018] The cubic boron nitride in the sintered compact obtained by this reaction sintering will be surrounded with Ti compound of the titanium boride formed of reaction sintering of cubic boron nitride and an oxygen content compound, and/or a titanium nitride, the detailed aluminum oxide 1 micrometer or less further formed of reaction sintering will distribute in a binder phase, and intensity and toughness will be raised further. The relation of this reaction sintering to cubic boron nitride has the desirable thing of 3 micrometers or more of mean particle diameters.

[0019] It is possible to use the carbonation object of Ti, Zr, and Hf which are the metal of 4a of a periodic table, a nitric oxide, and a charcoal nitric oxide, and the oxygen content compound for making reaction sintering perform has the carbonation object of Ti, a nitric oxide, and a desirable charcoal nitric oxide especially. Although it also influences the content of aluminum powder used simultaneously, the oxygen content of this oxygen content compound is 0.6 mols or less preferably about 0.8 mols or less, when the nonmetallic element in an oxygen content compound is made into one mol. This oxygen content compound has a non-stoichiometric composition to a desirable bird clapper, and its bird clapper is especially desirable from *****.

[0020]

[Function] By the aluminum oxide which consists of particle size of 1 micrometer or less formed of reaction sintering, and other binder-phase components, the sintered compact of this invention carries out the toughness of a binder phase, and the improvement operation in on the strength, and is carrying out the operation to which Ti compound of the titanium boride formed in the state where especially cubic boron nitride was surrounded, and/or a titanium nitride makes precise cubic boron nitride, a binder phase, and a boundary, and the operation which strengthens combination.

[0021] Moreover, the manufacture method of the sintered compact of this invention sets the big role with which cubic boron nitride induces reaction sintering to the oxygen content compound and aluminum which are used as a starting material, and is carrying out the operation to which an oxygen content compound induces a complex reaction called the reaction of an oxygen content compound and aluminum, the reaction of an oxygen content compound and cubic boron nitride, and the reaction of aluminum and cubic boron nitride especially.

[0022]

[Example] It blends with the composition shown in Table 1 using the cBN powder of 4 micrometers of mean particle diameters, the carbonation object powder of 1 micrometer of mean particle diameters, nitric oxide powder, aluminum powder of 1 micrometer of mean particle diameters, the carbide powder of Ti of 1 micrometer of mean particle diameters, nitride powder, the carbide powder of Hf, the nitride powder of Ta, the carbide powder of Zr, and 2Oaluminum3 powder of 0.5 micrometers of mean particle diameters, and preferential grinding of this is had and carried out with the ball made from cemented carbide, and a After having carried out die pressing of the end of mixed powder it obtained, fabricating it and making it a green compact, on 1×10^{-5} Torr and 850-degree C conditions, subsequently to extra-high voltage elevated-temperature equipment it installed, and it had on condition that the pressure of 5.5GPa, the temperature of 1500 degrees C, and the holding time for 30 minutes, and sintered [** paraffin processing was carried out, and], and this invention article 1-8 and the comparison article 1-4 were obtained.

[0023] In this way, this invention article 1-8 and the comparison article 1-4 which were obtained were measured according to the X diffraction, and the composition component was shown in Table 2. Moreover, in quest of the hardness and the fracture toughness value of these sintered compacts. it wrote together to Table 2. Next, when it had under the microscope and organization observation of a sintered compact was performed, this invention article 1, 4, and 6 had changed into the state where Ti compound surrounded cubic boron nitride, and the average layer thickness was about 1 micrometer. Moreover, the aluminum oxide of 0.1 micrometers - 0.2

micrometers of mean particle diameters was distributing this invention article 1-8 uniformly.

[0024]

[Table 1]

試料番号	配 合 組 成 (vol%)
本 発 明 品	1 50cBN - 35TiO ₂ C _{6.5} - 15Al
	2 60cBN - 22TiO ₂ C _{6.7} - 18Al
	3 60cBN - 25TiO ₂ C _{6.7} - 15Al
	4 60cBN - 25TiO ₂ N _{0.5} - 15Al
	5 50cBN - 35TiO ₂ N _{0.7} - 15Al
	6 50cBN - 27TiO ₂ C _{6.5} - 9HfC - 14Al
	7 60cBN - 18TiO ₂ N _{0.7} - 10TaN - 10Al
	8 50cBN - 25TiO ₂ N _{0.7} - 13ZrC - 12Al
比 較 品	1 50cBN - 35TiC - 7Al ₂ O ₃ - 8Al
	2 60cBN - 25TiN _{0.5} - 7Al ₂ O ₃ - 8Al
	3 60cBN - 30TiN - 10Al
	4 60cBN - 25Al ₂ O ₃ - 5TiC _{0.5} N _{0.7} - 10Al

[0025]

[Table 2]

試料番号	焼 結 体 組 成 (vol%)	硬 さ (Hk)	破壊靱性値 (MN/m ^{3/2})
本 発 明 品	1 44cBN - 29TiC - 16Al ₂ O ₃ - 8TiB ₂ - 3AlN	2620	8.2
	2 54cBN - 21TiC - 10Al ₂ O ₃ - 4TiB ₂ - 5AlB ₂ - 6AlN	3050	7.3
	3 56cBN - 24TiC - 9Al ₂ O ₃ - 5TiB ₂ - 6AlN	3010	7.5
	4 53cBN - 22TiN - 12Al ₂ O ₃ - 9TiB ₂ - 4AlN	3040	8.0
	5 46cBN - 34TiN - 8Al ₂ O ₃ - 4TiB ₂ - 3AlB ₂ - 5AlN	2670	7.3
	6 45cBN - 25TiC - 9HfC - 11Al ₂ O ₃ - 7TiB ₂ - 3AlN	2710	7.8
	7 58cBN - 17TiN - 10TaN - 6Al ₂ O ₃ - 5TiB ₂ - 4AlN	2980	7.1
	8 48cBN - 23TiN - 13ZrC - 7Al ₂ O ₃ - 4TiB ₂ - 5AlN	2660	7.4
比 較 品	1 48cBN - 35TiC - 9Al ₂ O ₃ - 5AlN - 3AlB ₂	2650	5.8
	2 58cBN - 26TiN - 2TiB ₂ - 9Al ₂ O ₃ - 5AlN	2980	6.2
	3 59cBN - 29TiN - 2TiB ₂ - 6AlN - 3AlB ₂	3020	6.5
	4 58cBN - 28Al ₂ O ₃ - 5TiC _{0.5} N _{0.7} - 5AlN - 4AlB ₂	3090	6.7

Subsequently, using this invention article 1-8 and the comparison article 1-4, the cutting examination by the

following conditions was performed and the result was shown in Table 3.

[0026] (A) **-ed [cutting test condition] material : SCN415 (HRC 60.9-61.7)

Periphery continuation dry-type cutting cutting speed: A cutting time until it is set to amount VB=of average flank wears0.2mm, or cutting time of a midcourse deficit : The amount of 150 m/min cuts : It sends 0.5mm. : 0.1 mm/rev chip configuration: TNMA160408 electrode holder : CTGNR2020 evaluation (in addition, VB is measured every 5min(s))

(B) **-ed [cutting test condition] material : FC30 (HB [210-230])

A cutting time until it is set to amount VB=of periphery continuation wet cutting cutting-speed average flank wears0.2mm, or cutting time of a midcourse deficit : The amount of 500 m/min slitting: It sends 0.5mm. : 0.15 mm/rev chip configuration: TNMA160408 electrode holder : CSBNR2020 evaluation : (in addition, VB is measured every 10min(s))

[0027]

[Table 3]

試料 番号		(A) 切 削 試 験		(B) 切 削 時 間	
		寿命迄の時間 (分)	損 傷 状 態	寿命迄の時間 (分)	損 傷 状 態
本 発 明 品	1	60	正常摩耗	210	正常摩耗
	2	50	正常摩耗	180	正常摩耗
	3	45	正常摩耗	150	正常摩耗
	4	70	正常摩耗	230	正常摩耗
	5	65	正常摩耗	160	正常摩耗
	6	65	正常摩耗	200	正常摩耗
	7	60	正常摩耗	210	正常摩耗
	8	55	正常摩耗	190	正常摩耗
比 較 品	1	35	正常摩耗	40	欠損
	2	30	欠損	70	正常摩耗
	3	20	欠損	60	欠損
	4	40	正常摩耗	120	正常摩耗

[0028]

[Effect of the Invention] The sintered compact of this invention has a high fracture toughness value compared with the conventional cubic boron nitride content sintered compact, and since it excels in a thermal shock resistance, the deficit-proof nature in an elevated temperature, oxidation resistance, etc., in the case of the sintered compact which becomes long lasting when it uses as a cutting tool especially by which cubic boron nitride was surrounded with Ti compound, there is at the inclination for the effect to become high more.